Job No.: 1505-94511 Ref.: DD 286179

Translated from German by the Ralph McElroy Translation Company 910 West Avenue, Austin, Texas 78701 USA

FEDERAL REPUBLIC OF GERMANY GERMAN PATENT OFFICE PATENT NO. DD 286 179 A5 EXCLUSION PATENT

Int. Cl.⁵:

C 11 D 1/94

C 11 D 3/37

Filing No.:

DD C 11 D / 324 289.5

Filing Date:

December 12, 1988

Date Granted:

January 17, 1991

DETERGENT FOR WOOL

Inventors:

Dr. Horst Seibt

Dr. Detlef Ballschuh Dr. Roland Ohme Dr. Leonhard Zastrow

DD

Applicant:

Akademie der Wissenschaften der

DDR

Otto-Nuschke-Strasse 22/23

Berlin, 1080, DD

Patent holder:

Akademie der Wissenschaften der

DDR

Zentralinstitut für Organische

Chemie

Berlin 1199, [DD]

Akademie der Wissenschafte der

DDR

Institut für chemische Technologie

Berlin 1199, DD

Representative:

Akademie der Wissenschaften der

DDR

Zentralinstitute für Organische

Chemie BfPN

Rudower Chaussee 5 Berlin, 1199, DD

Granted pursuant to §17, Section 1 Patent Act of the German Democratic Republic of October 27, 1983 in accord with the corresponding provisions of the Unification Treaty.

Keywords:

Detergent; detergent for wool; liquid formulation; surfactant combination

Abstract

The invention relates to a detergent for wool which contains, as a base surfactant, known nonionic surfactants which are combined with commercial anionic surfactants, sulfobetaine/multifunctional sulfobetaine sulfone mixtures, hydrotrope or hydrotrope mixtures and lower alcohols, polyvalent alcohols, ethylene glycols or diethylene glycol monobutyl ethers. This detergent formulation for wool possesses a good cleaning effect simultaneously with fiber finishing properties.

Claims

- 1. Detergent for wool, characterized in that it consists of
- 15-45 wt% of a nonionic surfactant, chosen from the group of polyoxyethylene adducts or polyoxypropylene-polyoxyethylene adducts or mixtures thereof,
 - 0.1-5 wt% of a nonionic surfactant, chosen from the group of sulfonates,
 - 2-6 wt% N-C₁₆H₃₃/C₁₈H₃₇ alkyl-N,N-bis(oxyethylene)amine with 5-15 EO units,
- 2-6 wt% N- $C_{16}H_{33}/C_{18}H_{37}$ alkyl-N,N-bis(oxyethylene)ammoniopropane sulfonate with 2.5-15 EO units,
 - 2-8 wt% of a multifunctional sulfobetaine sulfone mixture,
 - 2-10 wt% hydrotrope or mixture of different hydrotropes,
 - 10-20 wt% of an organic solvent or mixtures thereof,
 - 0-0.3 wt% of an optical brightener or mixtures thereof,
 - 0-0.3 wt% perfume and
 - 0-66.9 wt% of an additive or additive mixture and adjustment to 100 wt% with water.
- 2. Detergent for wool according to Claim 1, characterized in that one uses as nonionic surfactant, an ethoxylated fatty alcohol mixture having a chain length of C-9 to C-18 and an average EO content of 8-15 EO units, a C-8 to C-13 alkylphenylpolyoxyethylene with 8-15 EO units, or of industrial ethoxylated fatty alcohol mixtures, which were prepared by selective reduction of fatty acid mixtures with a high proportion of unsaturated acids while preserving the double bonds and, on average, present 6-18 C atoms, and have an average EO content of 5-

15 EO units, as well as C-12/C-14 alcohol mixtures with an average CO content of 3-5 units and an average EO content of 2-6 EO units.

- 3. Detergent for wool according to Claims 1 and 2, characterized in that as anionic surfactant, a C-9 to C-15 alkane sulfonate or C-12 to C-16 olefin sulfonate is used.
- 4. Detergent for wool according to Claim 1-3, characterized in that one uses, as multifunctional sulfobetaine sulfone mixture, reaction products made of maleic acid anhydride with fatty alcohols or fatty alcohol mixtures, ethoxylated fatty alcohols, ethoxylated fatty amines, fatty amines and polyethylene glycols having molecular weights of 300-5000, as well as the subsequent addition of 1,1-dimethyl-3-sulfinic acid methyl-4-sulfomethylpyrrolidinium betaine to this mixture, preferably the reaction product of maleic acid anhydride and industrial oxo alcohol having the average composition of $C_{13}H_{27}OH$, ethoxylated tallow fatty amine having the average composition of $C_{17}H_{35}N(EO_n)_2$ with 3 EO units in the molecule, polyethylene glycol having a molecular weight of 4000 and distilled industrial tallow fatty amine having the average composition of $C_{17}H_{35}NH_2$ as well as the subsequent addition of 1,1-dimethyl-3-sulfinic acid methyl-4-sulfomethylpyrrolidinium betaine to this mixture.
- 5. Detergent for wool according to Claims 1-4, characterized in that, as hydrotrope, short chain organic molecules are used with a cluster of polar groups such as dimethylaminomethanebisphosphonic acid, glucose, 1,1,3-trimethyl-4-sulfomethylpyrrolidinum betaine, 1,1-dimethyl-3-sulfinic acid methyl-4-sulfomethylpyrolidinium betaine, 1,1-dimethyl-3,4-disulfomethylpyrrolidinium betaine, citric acid, propanetrisulfonic acid, gluconic acid or mixtures thereof, preferably dimethylaminomethanebisphosphonic acid.
- 6. Detergent for wool according to Claims 1-5, characterized in that one uses, as inorganic solvents, lower alcohols such as ethanol, isopropanol and n-propanol, polyvalent alcohols such as glycerol and propanediol, or ethylene glycols such as triethylene glycol, or ethylene glycol monoethers such as diethylene glycol monobutyl ether, or mixtures thereof.
 - 7. Detergent for wool according to Claims 1-6, characterized in that as additive,
 - 0-2 wt% urea,
 - 0-0.1 wt% of silicone oil from the group of dimethylpolysiloxanes and
- 0-2 wt% of a graying inhibitor or mixtures of these additives, in that pH regulation is carried out with an industrial sodium hydroxide solution, ethanolamine or triethanolamine, and the adjustment to 66.9 wt% is made with water.
- 8. Detergent for wool according to Claim 1-7, characterized in that the pH regulation is carried out with an industrial sodium hydroxide solution, ethanolamine or triethanolamine to values of 6.5-7.

Field of application of the invention

The invention relates to detergents for wool, which, when used, present good application properties with regard to detergency in the low temperature range, fiber and fabric finishing, and color behavior.

Characteristic of the known state of the art

Liquid detergent formulations for treating natural and synthetic fibers as a rule have a pH of 5-8. They belong to the group of fine detergents or special detergents. In GB-PS 1,247,189, such detergent formulations are presented. They consist of the following components: ammonium lauryl sulfate, coconut fatty acid diethanolamide, ethoxylated lauryl alcohol with 7 EO units, hexylene glycol, perfume, neutral monoethanol citrate, citric acid and water. The pH can be regulated to 5-7 by different citric acid additions. In the preparation of these formulations one must ensure that no alkali or alkaline-earth metal ions occur, to prevent demixing and thus a reduction in the stability during the storage of these formulations. Examinations have also shown that the applications properties are then worsened.

Fine-fabric detergent formulations are usually builder-free in composition, because once the degree of soiling of these fiber fabrics is not that high, the soiling can be eliminated more easily, and in the detergent products used, to prevent damage to the fiber by the detergent, the pH is adjusted to approximately neutral. The application of this detergent product as a rule takes place at lower temperatures.

Liquid detergent formulations, whose composition is builder-free, have, for example, the following composition: sodium dodecylbenzene sulfonate, coconut fatty acid ethanolamine, laponite S – a nonionogenic surfactant, sodium sulfate and xylene sulfonate as hydrotrope (DE-OS 22,15,441).

In GB-PS 1,128,836, liquid fine-fabric detergent formulations are presented which, in particular, show the synergistic effect which occur when olefin sulfonate with a zwitterionic surfactant is used. The zwitterionic surfactant represents a carbobetaine type.

Stable, liquid, enzyme-containing washing and cleaning agents according to the patent CH-PS 548,446 have the following composition: linear C-18 alkylbenzene sulfonate, coconut alcohol ether sulfate, coconut fatty acid ethanolamide, ethanol, enzyme preparation (Alcalase) and water.

In the patent DE-OS 3,011,550, a liquid aqueous cleaning agent is protected which has the following general composition: a mixture of 50 parts by weight of a sulfated addition product of 1-5 mol EO to an n-C-12 alcohol and an n-C-14 alcohol, one or more anionic surfactants in combination, a betaine, preferably C-11 to C-17

alkylamidopropyldimethylcarboxymethylbetaine, a solvent and a solution enhancing agent, as well as a thickner, dye and perfume.

In US-PS 3,849,348, sulfobetaines are used as the main component, stearylsulfobetaine, coconut fatty acid amidosulfobetaine; in addition, one also uses in formulations the corresponding carbobetaines in combination with the sulfobetaines. These betaines are then usually combined with nonionic surfactants.

In DE-OS 21,54,973, liquid detergents are offered which consist of a combination of N-alkylamicopropyldimethylbetaine (C-10 to C-16) and Na N-(2-hydroxyhexadecyl)-N-methyl taruinate.

JP-PS 70,18,987 presents liquid detergent combinations; they consist of alkyl ether sulfate and dodecyldimethylaminoacetate in a ratio by weight of 5:1, the rest is ethanol, perfume and water.

According to JP-PS 70,33,780, liquid detergents are obtained which consist of aliphatic alpha-olefin sulfonates and which are combined with Na bis(ethylhexyl) sulfosuccinate, ethanol, urea, ammonium chloride and water. With this detergent, natural and synthetic fibers can be washed, however, the application properties which one expects from a special detergent cannot be achieved with this composition.

In DE-OS 34,27,078, a detergent for delicate textiles, wool and silk is presented. It consists of alkyl ether sulfate Na salt (alkyl: C-12 to C-18), fatty acid monoethanolamide in a ratio of 5:1, and emulsified silicone defoaming agent, as well as a bactericide, a small amount of citric acid as complexing agent for heavy metals and glycerol. The cited detergent formulations, which are suitable for cleaning natural fibers, in particular wool, have the drawback that they cannot be used with highly soiled fabrics, that, during usage, one must work in addition with fabric finishing soft rinsing agents, and that, if these detergent formulations are frequently used, the color of dyed wool fabric fades.

Purpose of the invention

The purpose of the invention consists in developing a liquid detergent formulation for wool which is chemically and physically stable and safe from the ecological point of view, and which possess good application properties with regard to detergency, fiber finishing and color behavior.

Presentation of the substance of the invention

The invention is based on the problem of finding a detergent formulation for wool with good application properties with regard to detergency, fiber finishing and color behavior.

The problem was solved using the detergent formulation for wool according to the invention which has the following composition.

- 15-45 wt% of a nonionic surfactant, chosen from the group of polyoxyethylene adducts or polyoxypropylene-polyoxyethylene adducts or mixtures thereof,
 - 0.1-5 wt% of a nonionic surfactant, chosen from the group of sulfonates,
 - 2-6 wt% N-C₁₆H₃₃/C₁₈H₃₇ alkyl-N,N-bis(oxyethylene)amine with 5-15 EO units,
- 2-6 wt% N- $C_{16}H_{33}/C_{18}H_{37}$ alkyl-N,N-bis(oxyethylene)ammoniopropane sulfonate with 2.5-15 EO units,
 - 2-8 wt% of a multifunctional sulfobetaine sulfone mixture,
 - 2-10 wt% hydrotrope or mixture of different hydrotropes,
 - 10-20 wt% of an organic solvent or mixtures thereof,
 - 0-0.3 wt% of an optical brightener or mixtures thereof,
 - 0-0.3 wt% perfume and
- 0-66.9 wt% of an additive or additive mixture, pH regulation with an industrial sodium hydroxide solution, ethanolamine or triethanolamine, and adjustment to 100 wt% with water.

As additives for the detergent for wool one can use:

- 0-2 wt% urea,
- 0-0.1 wt% of a silicone oil from the group of dimethylpolysiloxanes and
- 0-2 wt% of a graying inhibitor.

As nonionic surfactant one can use ethoxylated fatty alcohol mixtures having a chain length of C-9 to C-18 with an average content of 8-15 EO units, a C-8 to C-13 alkylphenolpolyoxyethylene with 8-15 EO units, or industrial ethoxylated fatty alcohol mixtures which were prepared by selective reduction of fatty acid mixtures which have a high content of unsaturated acids with preservation of the double bonds, and which present on average 16-18 C atoms and an average EO content of 5-15 EO units, as well as C-12/C-14 alcohol mixtures with an average PO content of [PO]3-5 units and an EO content of 2-6 EO units.

C-9 to C-15 alkane sulfonates or C-12 to C-16 olefin sulfonates can be used as anionic surfactants.

As hydrotropes for the detergent formulations for wool, lower molecular weight organic compounds with a cluster of polar groups are suitable according to the invention. One can use, in particular, the following compounds:

- dimethylaminoethanebisphosphonic acid,
- citric acid,
- propanetrisulfonic acid,
- propane-1,3-disulfone-2-sulfinic acid,
- 1,1,3-trimethyl-4-sulfomethyl-pyrrolidinium betaine,

- 1,1-dimethyl-3-sulfinic acid methyl-4-sulfomethylpyrrolidinium betaine,
- 1,1-dimethyl-3,4-disulfomethylpyrrolidinium betaine,
- glucose, and
- gluconic acid.

Their mixtures as well can be used.

The multifunctional sulfobetaine sulfone mixture can be prepared in a "one-pot method" by joint and simultaneous reaction of maleic acid mono-N-alkylamides and maleic acid monoalkyl esters with a sulfobentaine sulfinic acid. Thus, for example, a multifunctional sulfobetaine mixture can be synthesized by the reaction of maleic acid anhydride with fatty alcohols or fatty alcohol mixtures, ethoxylated fatty alcohols, ethoxylated fatty amines and polyethylene glycols having molecular weights of 3000-5000, with the subsequent addition of 1,1-dimethyl-3-sulfinic acid-methyl-4-sulfomethylpyrrolidinium betaine to this mixture.

The organic solvents are used to produce homogeneous detergent formulations for wool and, as additives, they also influence the cleaning effect. Moreover, the foam can be regulated to a certain extent. For use in the formulations according to the invention, one can consider lower alcohols such as ethanol, isopropanol and n-propanol, polyvalent alcohols such as glycerol and propanediol or ethylene glycols such as triethylene glycol, or ethylene glycol monoethers such as diethylene glycol monobutyl ether, or mixtures thereof.

It was surprisingly found that the detergent formulations for wool present, in addition to their good cleaning effect, even with strongly soiled woven fabrics, a fiber softening effect, which, in the case of colored fibers, results in a color brightening effect, and prevents matting of the wool fibers.

The detergent formulation for wool can be used both for washing by hand and for washing in a machine. For use in washing machines, a defoaming additive is added to the formula, and it is particularly appropriate to use, in the detergent formulations for wool, silicone oils of the dimethylpolysiloxane type. In the process, the application properties of the formulation are not negatively influenced.

During the formulation studies and examination of the cleaning effect of woven fabrics it was noted that derivatives of phosphorylated starch are particularly suitable as graying inhibitors. The reaction product of potato starch and sodium cyclotriphosphate presented very good properties with respect to their capacity for being incorporated in the formulation, the stability of the latter and graying inhibition.

High degrees of soiling, which usually can only be eliminated by alkaline formulations which damage the wool fiber, are removed with this detergent formulation for wool.

Advantages in the usage of this detergent formulation for wool are:

- the nonionic [surfactant] which is used as the base surfactant is a commercial product,

- 1 wt% urea,
- 0.6 wt% phosphorylated starch product,
- 0.02 wt% optical brightener,
- 0.15 wt% perfume oil,
- 0.2 wt% dimethylpolysiloxane,

Adjustment to 100: the pH is adjusted with triethanolamine to 6.0 and the dilution to 100 wt% is carried out with water. The formulation so prepared is suitable for use in washing machines.

Example 3

- 17 wt% nonylphenylpolyoxyethylene with [illegible] EO units
- 2 wt% alkane sulfonate (C-9 to C-15 alkyl chain mixture),
- 6 wt% N-C₁₆H₃₃/C₁₈H₃₇ alkyl-N,N-bis(oxylethylene)amine with 5 EO units.
- 3 wt% N-C₁₆H₃₃/C₁₈H₃₇ alkyl-N,N-bis(oxyethylene)ammoniopropane sulfonate with 3 EO units,
 - 5 wt% multifunctional sulfobetaine sulfone mixture,
 - 2 wt% dimethylaminomethanebisphosphonic acid,
 - 5 wt% 1,1,3-trimethyl-4-sulfomethylpyrrolidinium betaine,
 - 10 wt% 1,2-propanediol/triethylene glycol mixture in a ratio by weight of 1:1.5,
 - 0.6 wt% phosphorylated starch product,
 - 0.02 wt% optical brightener,
 - 0.15 wt% perfume oil,
 - 1 wt% urea,
 - 0.2 wt% dimethylpolysiloxane and

Adjustment to 100: the pH is adjusted with 33% industrial sodium hydroxide solution to 6.5 and then diluted to 100 wt% with water.

Example 4

The composition of Example 4 corresponds to the Example 1; instead of dimethylaminomethanebisphophonic acid, 1,1-dimethyl-3-sulfinic acid methyl-4-sulfomethylpyrrolidinium betaine was used in the same ratio by weight.

Example 5

Composition as in Example 2, except that the dimethylaminomethanebisphosphonic acid was replaced by citric acid at the same weight %.

			ej .
			!
•			